ON THE COPPER AGE IN ANCIENT CHINA I.

By Tsurumatsu DŌNO.

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It has been generally believed that, in ancient civilized lands, the material civilization began at the age, in which stone implements were made use of, then entered into the metallic age and has come up to our days, passing through the ages of copper, bronze and iron implements, time after time. Now, it has also been stated by the relics unearthed from old sites that in ancient China there existed the stone age. As to the beginning of the bronze age in China, it is now supposed to date back to remote antiquity, though its absolutely exact period of appearance has been yet unknown. This fact is certified by a good deal of remains of those days which now exist, and it has been properly recognized that, in Chou dynasty (周代), various kinds of very exquisite bronze implements had already been manufactured. Further, in Chou-Li K'ao-Kung-Chi (周禮考工記) which is considered to be written in former Han (前漢) or before that dynasty—namely Ch'in dynasty (秦代) or Chan-Kuo period (戰國時代)—the following sentence can be found:—

金有六齊。六分其金而錫居一謂之鐘鼎之齊。五分其金而錫居一謂之
斧斤之齊。四分其金而錫居一謂之戈戟之齊。三分其金而錫居一謂之
大刃之齊。三分其金而錫居二謂之削殺矢之齊。金錫半謂之鑒燧之齊。

The Chinese classics above cited, displays the following meaning —that is, for bronze there are six mixtures according to their uses.

6	Parts	of copper	and	1	part of tin,	is used for bells and vessels etc.
5	,,	,,		1	,, ,,	socketed axe-heads.
4	,,	,,		1	,, ,,	halberds.
3	,,	,,		1	,, ,,	swords.
5	,,	,,		2	parts ,, ,,	arrow-heads.
1	Part ,,	,,		1	part ,, ,,	plane or concave mirrors.(1)

This sentence makes us to infer that, in those days, according to the purposes in which bronze was employed, the proportions between

(1) Metallic tools which were used for taking fire focussing the sun-light.

Chin[1] (金) and tin in bronze were astonishingly well studied, and it may be said that the proportions of those two metals and the way by which those alloys were employed, mentioned in above sentence, are almost quite right from the standpoint of the alloyage of the recent time, although there exist a few points to be corrected. In another chapter of Chou-Li K'ao-Kung-Chi (周禮考工記), the following sentence can be found:—

凡鑄金之狀. 金與錫黑濁之氣竭黃白次之。黃白之氣竭青白次之。青白之氣竭青氣次之。然後可鑄也。

This shows us the casting process of bronze in those days. In these words, we can find that even in those ancient times, the coloured flame reaction was properly utilised to decide the best chance for casting (casting temperature): namely, ancient Chinese founders performed the casting at the time in which copper was molten entirely and evolved the blue flame of copper.

Conclusively, we can say that at the time in which Chou-Li K'ao-Kung-Chi (周禮考工記) was written, they had already possessed quite advanced knowledge about bronze. Besides this, it has been considered that iron weapons in China were appeared at first time at the end of Ch'un-Ch'iu dynasty (春秋時代) or at the beginning of Chan-Kao period (戰國時代), and gradually increasing the use of them. And the age in which the most parts of weapons were made of iron, was considered to be about at the end of former Han dynasty (前漢代); therefore we can conclude that during the intervals of Ch'un-Ch'iu dynasty (春秋時代), Chan-Kao period (戰國時代), Ch'in dynasty (秦代) and the upper age of former Han dynasty (前漢代) there was bronze-iron age, and after the end of former Han dynasty (前漢代) the pure iron age in China first took its appearance. In archaeology, as a rule, the ages of stone, copper, bronze and iron being classified according to the materials used for weapons, of course it must be said that bronze was not given up to use for every tools except weapons even after the end of former Han dynasty (前漢代).

As was described above, the existence of the stone and the bronze age in ancient China has been admitted with certainty. But the exis-

(1) Chin (金)—Here Chin means not gold but copper, in ancient China the whole metals were denoted by this letter Chin, and it was classified by colour into three species so-called San-P'in (三品)—that is, Huang-Chin (黃金), Po-Chin (白金) and Ch'ih-Chin (赤金)—and a little after, into five classes called Wu-Chin (五金)—namely Huang-Chin (黃金), Po-Ch n (白金), Ch'ih-Chin (赤金), Ch'ing-Chin (靑金) and Hei-Chin (黑金) or Hsüan-Chin (玄金). But, in general with a few exceptions, it also means copper alone. Perhaps copper was the most universal and representative kind of metals at that times; therefore copper was denoted by this letter Chin (金).

tence of the copper age in China has been considered in question, and even if it has really existed, its annalistic age would be beyond our imagination, on account of the want of copper implements which have never been discovered up to the present time (the word of copper does not mean chemically pure copper, but it means copper which is not artificially mixed with tin. Therefore it is allowable for the existence of other metals than tin, as impurities or from other standpoints).

As is well known, however, many remains of copper implements were discovered in ancient Egypt and other civilized lands, and it is said that in Egypt copper implements were used during long times, but this metal having been found too soft, several methods of copper-hardening were devised by Egyptian and after long and elavorated studies, bronze was at last brought into the world. In ancient China, therefore, the appearance of the bronze age after the stone age, skipping over the copper age, as is generally considered, seems somewhat improper, regarded from the orders of transition of utilization of metals. Taking these points in consideration, author has always suspected that the copper age must also have existed in China like in Egypt, although it has not been confirmed.

Fig. 1. Specimen A.

Fig. 2. Specimen B.

Fig. 3. Specimen C.

Quite recently author could have an occasion to carry out chemical studies of several crude spear-heads (Figs. 1, 2 and 3), for the kind deliverance of which he is very much indebted to the Archaeological

Institute of the Faculty of Literature of the Tokyo Imperial University. These spear-heads closely resemble with the relics recently unearthed from Yin site in Ho-Nan Province (河南省殷墟) in China. The results of the chemical analyses showed that these ancient Chinese spear-heads contain no significant amount of tin (indeed we could detect the metal only by arc spectral analysis, but as very faint lines). Now, author can conclude that these spear-heads must rather be called copper implements than bronze ones and thus he could here confirm that, in ancient China, there existed also the copper age like in ancient Egypt and other civilized lands. This will be in no less interest on the cultural history of China.

The results of the chemical analyses are as follows:—

	Specimen A	Specimen B	Specimen C
Sample (gr.)	0.4770	0.4266	0.5020
Copper (%)	91.36	72.68	57.17
Lead (%)	2.90	22.38	26.78
Iron (%)	1.42	2.12	1.05
Arsenic (%)	trace	0.80	trace
Silver (%)	0.10	0.30	0.05
Gold (%)	trace	trace	trace
Tin (%)	trace	trace	trace
Totals (%)	95.78	98.26	85.05

As will be seen in these results of chemical analyses, the total values are considerably less than 100%; among these, the specimen C is only about 85% in total. Author believes that this is due to the oxides which goes far into the inner part of the material and, there-

Fig. 4. Specimen A (Surface).

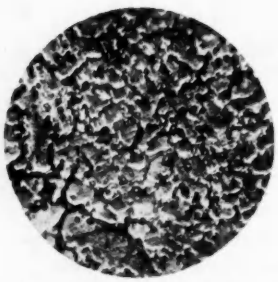

Fig. 5. Specimen A (Etched surface).

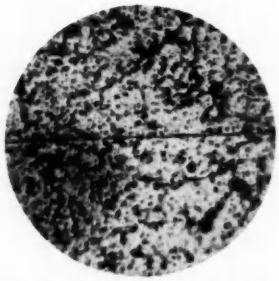

Fig. 6. Specimen A (Cross section).

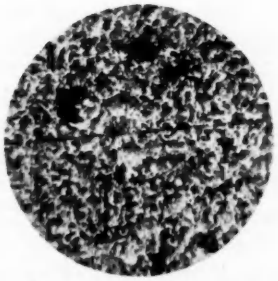

Fig. 7. Specimen A (Etched cross section).

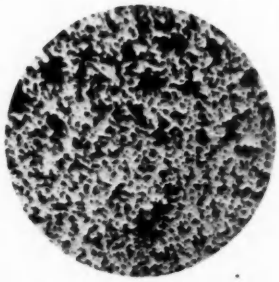

Fig. 8. Specimen B (Surface).

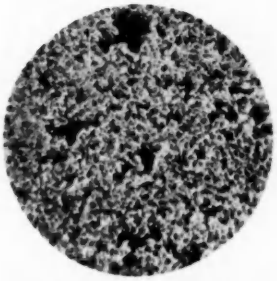

Fig. 9. Specimen B (Etched surface).

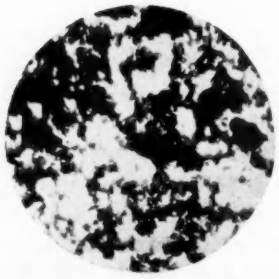

Fig. 10. Specimen C (Surface).

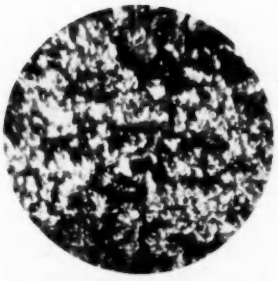

Fig. 11. Specimen C (Etched surface).

fore, a considerable amount of oxygen should be added to the elements above analysed. This can also be confirmed by the metallographical photograms (enlarged 100 times and etched by the solution of ammoniacal hydrogen-peroxide). It may be considered that the oxides in these specimens were produced by the following two causes: (1) as the technique of casting was still in its infancy in those days, oxidation

was not properly prevented at the time of melting, and (2) the materials have passed so long time as many thousand years, so that oxidation took place unartificially.

As for lead which is contained often in considerable quantities in the samples, it is hardly possible to think that it came from copper ores and it must rather be considered that this metallic element was artificially added in order to increase the fluidity of molten copper and to make the casting more easy. It will be no doubt that the other metals than copper and lead detected in the samples are contained as impurities which were impossible to be eliminated by the primitive metallurgical technique of those ancient days.

In conclusion, the author expresses his sincere gratitude to Prof. Dr. Y. Shibata, Prof. Dr. S. Katō and Prof. Dr. K. Kimura for their kind guidances, and to Prof. Dr. Y. Harada, Dr. K. Komai and Dr. N. Egami in the Archaeological Institute of the Faculty of Literature of Tokyo Imperial University, who offered the invaluable specimens for his chemical research, and also to Prof. Dr. T. Mishima for the trouble of taking the metallographical photographs.

Summary.

(1) Three specimens of ancient Chinese spear-heads which are said unearthed from Yin site (殷墟) were analysed, and it was found that they consist mainly of copper added with certain quantities of lead and contain no significant amount of tin.

(2) From the chemical studies, all these spear-heads are by no means of bronze and they are regarded as the first pure copper implements ever discovered in China.

(3) The prevailing opinion which negates the existence of the pure copper age in ancient China must thus be abandoned, and the existence of the copper age in China must be admitted.

(4) It is supposed that if these specimens were actually manufactured in Yin dynasty (殷代), the pure copper age in China existed at about Yin dynasty (殷代), and the beginning of the bronze age followed that age.

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A SPECTROCHEMICAL STUDY ON THE CHEMICAL CONSTITUTION OF A REACTION PRODUCT BETWEEN CENTRALITE AND GASEOUS NITROGEN PEROXIDE. DINITRODIPHENYLETHYLUREA.

By Kôiti MASAKI.

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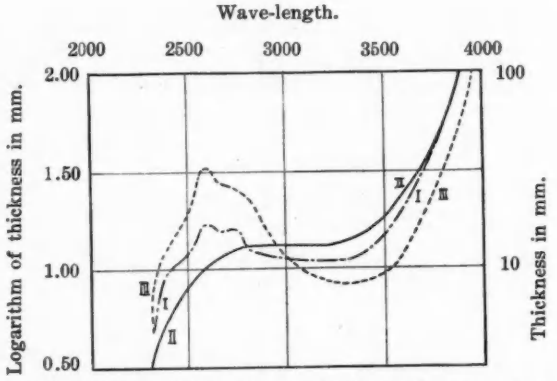
Diphenyl-diethyl-urea, known as "CENTRALITE" (C/L), is used in several countries as a good gelatinizer or stabiliser for the smokeless powders and is now investigated in many explosives laboratories in the world. The great stabilizing effect of this substance is no doubt due to reaction of it with formation of stable nitrocompounds, preventing the injurious action of NO_2 gas and its acids produced by the spontaneous decomposition of nitroglycerine and nitrocellulose. From the stability point of view, it is an interesting and important problem, to see whether tetranitrocentralite is formed or not by the reaction between centralite and NO_2 gas at room temperature. In the Note,(1) published in 1926, M. A. Apard reported on the formation of tetranitrocentralite which was obtained in a very small quantity as deep yellow powder by crystalizing the residue, produced with extraction by benzene solution, with ethyl alcohol. It is, however, doubtful whether the yellow powder is really tetranitrocentralite or not, because of the very small quantity. The author carried out the reaction between NO_2 gas and powdered centralite almost in the same manner, the time of the reaction being a little longer, and was able to separate a small quantity of yellow powder from a dark reddish, syrupy mass of the reaction product by treating with benzene. This powder crystallized from acetone as minute thin plates, melting at 207–210°C., somewhat different from the melting point (175°C.) of tetranitrocentralite.

The author started to study the absorption spectra of centralite, dinitrocentralite, tetranitrocentralite and the sample in question. The following figure shows a comparison of the absorption curves. Optical behaviours of the unknown compound resemble to that of dinitrocentralite, the absorption maximum of which is observed at 3200Å, while that of the former at 3350Å. On the other hand, the tetranitrocentralite is found to show no selective absorption. The small difference between absorption spectra of the unknown substance and dinitro-

(1) *Mém. Poudres*, **22** (1926), 181.



I. Dinitrodiphenyldiethylurea (0.0001% Alcoholic solution).
II. Tetranitrodiphenyldiethylurea (,,).
III. Unknown substance (,,).

Fig. 1.

centralite has been investigated position and number of nitrogroups.

Nitrogen content in the unknown substance determined by micro-analysis (micro-duma.) is given below.

Subst. = 2.20 mg.; N_2 = 0.319 c.c. at 26.0°C and 759 mm. Found: N = 16.6 %.

The relation between number of nitrogroups and nitrogen percentages in nitro-compounds of centralite is shown in the following table.

	mono.	di.	tri.	tetra.
N%	13.59	15.63	17.81	18.75

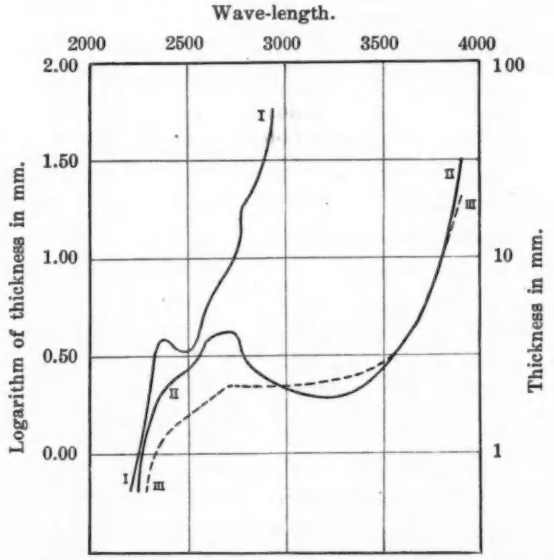
Thus the new substance can hardly be expected to be other than dinitro- or trinitro-derivative. The position of nitrogroup in a benzene ring accompanied with an acylimide group is, as a rule, ortho- or more likely para-position in the reaction at ordinary temperatures. In the case of the nitration of centralite and also in the reaction between NO_2 gas and centralite, the easiest product is sym.-*p*-dinitrocentralite; and then, with regard to the structure of the compound in question, all possible cases of di- and tri-nitrocentralites, except meta-structures and extremely unsymmetrical nitrocompounds which are improbable, are only the following.

(1) 4-4′-dinitro C/L. (Paraposition in a nucleus).
(2) 2-2′-dinitro C/L., 2-6-2′-trinitro C/L. (Orthposition in a nucleus).
(3) 2-4-4′-trinitro C/L., 2-4-2′-trinitro C/L. (Ortho- and para-position in a nucleus).

A relationship between these chemical constitutions and absorption curves has been studied. Intensity of the absorption band in the case of ortho-compound is feebler and the form is not simple compared with para-compound as Figs. 4 and 5 show, while the unknown compound in question has simply a deep and wide absorption band. From this point, it is not possible to consider that it should be ortho-compound as the 2nd.

The hypochromic influence of two or three nitrogroups takes mutually metaposition from the same optical behaviours of 2-4-2′-4′-tetranitrocentralite (Fig. 2), 2-4-dinitrophenylurethane (Fig. 3), 2-4-6-trinitrobenzene,[1] and 2-4-6-trinitroacetanilide (Fig. 4), so that the compound is not the 3rd type. There remains only the structure of the 1st type, in which each nitrogroup takes para-position for acylimide groups from the position of absorption band and its extinction coefficient, although it is not 4-4′-dinitrocentralite.

As for light absorption some para-nitro aromatic compounds with

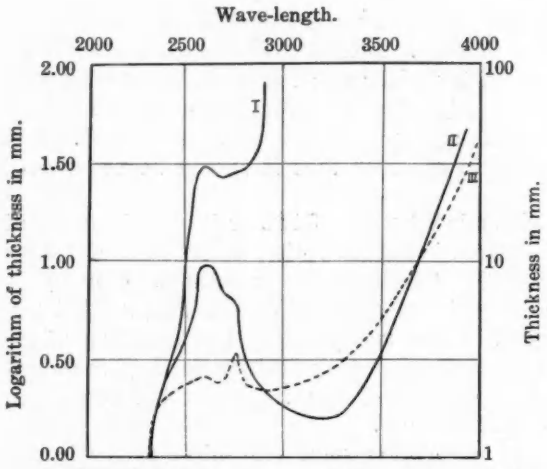


I. Diphenyldiethylurea (0.001 mol. in alcohol).
II. *p*-Nitrodiphenyldiethylurea (,,).
III. 2-4-2′-4′-Tetranitrodiphenyldiethylurea (,,).

Fig. 2.

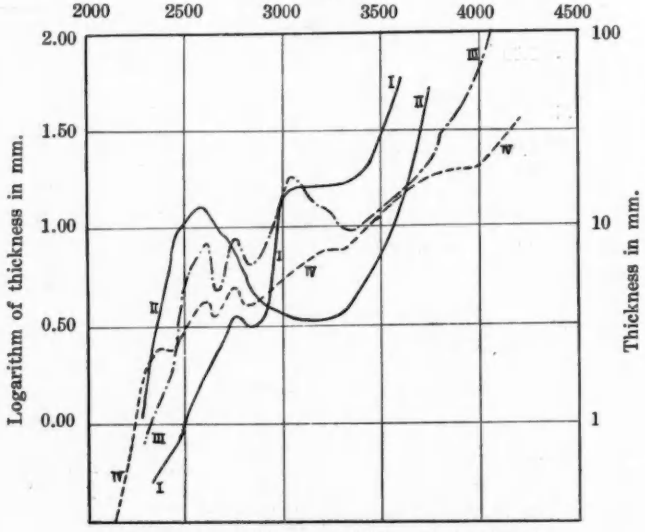
(1) *J. Chem. Soc.*, **103** (1913), 2085. *Ber.* **42** (1909), 2119; **43** (1910), 1662; **52** (1919), 493.

Fig. 3.



I. Phenylurethane (0.001 mol. in alcohol).
II. *p*-Nitrophenylurethane (,,).
III. 2-4-Dinitrophenylurethane (,,).

Fig. 4.



I. *m*-Nitracetanilide (0.001 mol. in alcohol).
II. *p*-Nitracetanilide (,,).
III. *o*-Nitracetranilide (,,).
IV. 2-4-6-Trinitracetanilide (,,).

acylimide group are found to be almost the same as the following table shows.

	Wave length	log ε.
p-Nitroacetanilide	320 m.μ.	ca. 3.5
p-Nitrophenylurethane	320 ,,	,, 3.8
Sym.-*p*-dinitro C/L	325 ,,	,, 3.8
Unknown compound	335 ,,	,, 3.8

These facts indicate that its formula is of a paranitro structure, and only small difference between unknown compound and dinitro C/L, which has more hypochromic influence than the former, may not be the influence of nitrogroup, but that of C_2H_5-group when compared with *p*-nitroacetanilide and *p*-nitroethylacetanilide (Fig. 5). From the above considerations, the unknown compound might be dinitrodiphenylethylurea or dinitrodiphenyl-urea, one or two of ethyl-groups being expelled from dinitrocentralite. Checks and determinations have been carried out by measurements of molecular weight and microanalysis of elements in the constituents. By Rast's method, the following results have been obtained.

Camphor	Sample	Temp. depres.	Mol. wt.
0.0924 gr.	0.0044 gr.	7.6°C.	3.1×10^2
0.0889 gr.	0.0053 gr.	9.9°C.	3.0×10^2

These values being less than those of dinitrocentralite, the structure of which, excluding ethyl-group, is also probable, and there remains two cases as given below.

	Mol. wt.
Dinitrodiphenylethylurea	330
Dinitrodiphenylurea	302

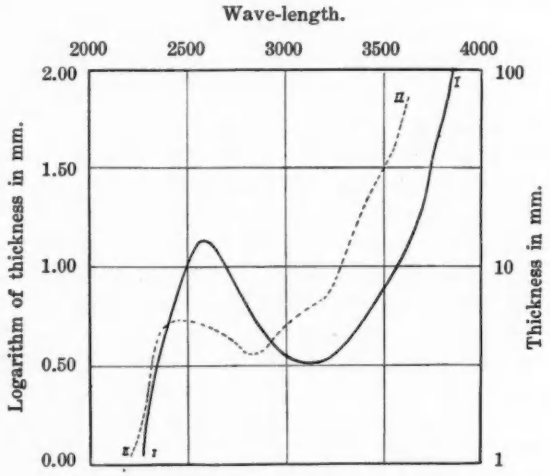
The percentages of the elements of these compounds are the following.

Calc. for	C	H	N	O
Dinitrodiphenylethylurea ($C_{15}H_{14}N_4O_5$)	54.6	4.24	17.0	24.2
Dinitrodiphenylurea ($C_{13}H_{10}N_4O_5$)	51.6	3.32	18.5	26.5

The result of the analysis of the sample is given below.

Anal.: Subst. = 4.54; CO_2 = 9.05; H_2O = 1.98 mg.

Found: C = 54.3; H = 4.8; N = 16.6 %.



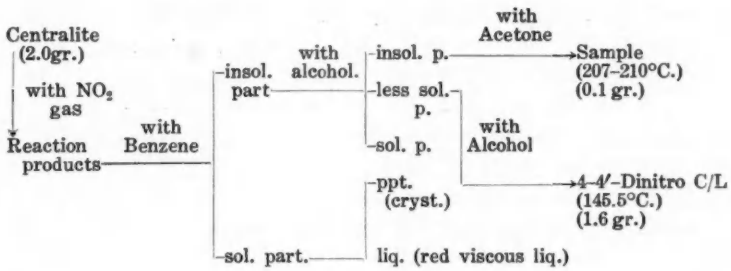
I. *p*-Nitracetanilide (0.001 mol. in alcohol).
II. *p*-Nitroethylacetanilide (,,).

Fig. 5.

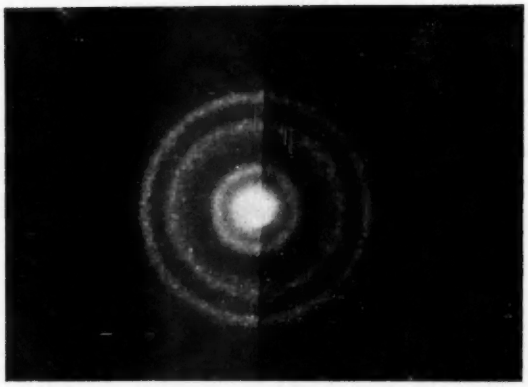
These are quite coincident with that of dinitrodiphenylethylurea. By these results and identification of that obtained by the synthesis which will be described later, the high melting point compound from centralite has been proved to be the dinitrodiphenyl-ethyl-urea.

Experimental Part.

Formation and Separation of the Sample. When NO_2 gas, diluted with air, was introduced in a bottle, containing 2.0 gr. of powdered centralite, the latter readily converted, from surface inward, into a viscous liquid of dark greenish colour, which turned brownish after allowing to stand overnight. This operation was repeated throughout a month or so, until no more reddish brown gas of NO_2, remained unchanged, and the viscous liquid partially solidified. On the mass of the products, the fractional separation was carried out with benzene, then with alcohol, and 5% of the sample (0.1 gr.) was obtained from the insoluble part in benzene and the other part was almost dinitrocentralite that was 80% corresponding to the initial substance. The process of the separation is given in the following table.



Sample obtained from the part insoluble in benzene and in alcohol, crystallized from acetone solution, consisted of yellow very thin plate crystals melting at 207–210°C., while that obtained from alcohol was faintly greenish yellow powder before recrystallisation. It is hardly soluble in ordinary solvents, especially in benzene, slightly soluble in small amount in acetic acid and acetone. The X-ray photograph obtained by Debye's method is shown in the following figure.



X-ray photo. of unknown subs. ×0.7
(Anticathode: Cu. dist. = 50 mm.)

Fig. 6.

4-4′-Dinitro-diphenyl-ethylurea. This substance was prepared by nitration of ethyldiphenylurea, which was obtained from phenylethylureachloride and aniline, at the temperature not exceeding 15°C. Twice recrystallisations with acetone suffice to render the raw product quite pure as crystals melting at 213.2–213.5°C.

Anal.: Subst. = 7.353; CO_2 = 14.62; H_2O = 3.26 mg.
Subst. = 1.921 mg.; N_2 = 0.287 c.c. at 23.0°C. and 775.3 m.m.
Found: C = 54.3; H = 4.9; N = 16.9%.
Calc. for $C_{15}H_{14}N_4O_5$: C = 54.6; H = 4.2; N = 16.9 %.

Properties.—Very thin plate of yellow colour, insoluble or hardly soluble in ordinary solvents, only soluble in hot acetone. The absorption maximum was observed at 335 m.μ. Both in the absorption spectrum and X-ray photograph, the substance bears excellent resemblence to the sample obtained from C/L.

4-4′-Dinitrodiphenyldiethylurea. Centralite dissolved in glacial acetic acid was nitrated with nitric acid (sp. gr. 1.4) at a temperature not exceeding 15°C. and the product was crystallized from glacial acetic acid, then recrystallized from alcohol (M.P. 145.5°C.). In 0.001 mol alcoholic solution, the absorption maximum was observed at 325 m.μ.

2-4-2′-4′-Tetranitrodiphenyldiethylurea. This substance was obtained by nitration of centralite by conc. nitric acid (sp. gr. 1.5) at about 10°C. The product was crystallized from glacial acetic acid (M.P. 175°C.). In the 0.001 mol alcoholic solution, no absorption band was observed except an inflection in the absorption curve (Fig. 2).

Phenylurethane. The sample was prepared from aniline and diethylcarbonate which was obtained by the reaction between ethylalcohol and phosgene, $COCl_2$. The product melted at 51.5°C. The absorption maximum was observed at 269 m.μ (Fig. 3).

***p*-Nitrophenylurethane.**[1] By introducing nitric acid into etheric solution of phenylurethane, the sample was prepared (M.P. 127°C.), the absorption maximum of which was observed at 325 m.μ. (Fig. 3).

2-4-Dinitrophenylurethane.[2] This substance was prepared by dissolution of phenylurethane in nitric acid (D. 1.5) at low temperature (M.P. 110–111°C.). In its absorption curve only slight maxima were observed at 268 m.μ. and 288 m.μ. (Fig. 3).

***o*-Nitracetanilide. *m*-Nitracetanilide.** Both nitracetanilides were prepared from *o*-nitraniline[3] or *m*-nitraniline[4] and acethylchloride at ordinary temperature. The former melts at 92–93°C., and the latter

(1) *Ann.*, **233**, 9.
(2) *Rec. trav. chim.*, **10**, 141.
(3) *Ber.*, **39** (1906), 3903.
(4) *Ann.*, **57** (1846), 217.

at 145°C. These substances showed the following absorption maxima.

o-nitracetanilide	266 m.μ.	283 m.μ.	333 m.μ.
p-nitracetanilide		284 m.μ.	332 m.μ.

p-Nitracetanilide.[1] **p-Nitroethylacetanilide.**[2] By nitration of acetanilides, these two samples were obtained, the former melting at 207°C., the latter at 117–118°C. They show each a wide absorption band, the maximum of the former being observed at 321 m.μ., while that of the latter at 285 m.μ. (Fig. 5).

2-4-6-Trinitroacetanilide.[3] The substance was prepared from picramide and acetylchloride. It decomposed at 208–211°C.

Anal.: Subst. = 3.950 mg.; N_2 = 0.704 c.c. at 24.0°C and 766.1 m.m.

Found: N = 20.60 %. Calc. for $C_7H_6N_4O_7$: N = 20.68 %.

In its absorption curve four slight maxima were observed at 243 m.μ., 265 m.μ., 283 m.μ. and 311 m.μ. Three nitrogroups mutually in meta-positions in a benzene ring shows the hypochromic influence (Fig. 4).

In conclusion, the author wishes to express his gratitude to Prof. Y. Shibata for his suggestions and advice in connection with the spectrochemical part, to Prof. N. Yamaga for his interest in this work and to Mr. H. Marue for the trouble of taking the X-ray photographs.

Summary.

1. In 1926 M. A. Apard reported the formation of tetranitrocentralite by the reaction of nitric peroxide upon centralite at ordinary temperature. Owing to want of his experimental data, because of the very small quantity of his sample, it seemed however so doubtful that the author was tempted to set out this investigation, and determined its chemical structure by the spectrochemical and microanalytical methods.

2. Absorption spectra have been studied on the following ten substances. 4-4′-Dinitrodiphenyldiethylurea, 2-4-2′-4′-tetranitrodiphenyldiethylurea, *p*-nitrophenylurethane, 2-4-dinitrophenylurethane, *o*-nitroacetanilide, *m*-nitroacetanilide, *p*-nitroacetanilide, *p*-nitroethylacetanilide, 2-4-6-trinitroacetanilide and 4-4′-dinitroethyldiphenylurea.

(1) *Ber.*, **9**, 775. *Ann.*, **197**, 83.
(2) *Ber.*, **16**, 31. *Ber.*, **17**, 267.
(3) Compare *Ber.*, **41**, 3092.

3. As to the chemical constitution of the reaction product of higher melting point obtained from centralite, it has been proved to be dinitrodiphenylethylurea, which crystallizes from acetone solution in a form of very thin plates of yellowish colour, melting at 213.2–213.5°C., and hardly soluble in ordinary solvents.

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A CONTRIBUTION TO THE FISH OIL THEORY OF THE ORIGIN OF PETROLEUM FROM A STUDY OF BRINE WATERS FROM WIDELY DIFFERENT OIL FIELDS IN JAPAN.

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Introduction. The widely known fact that brine water and petroleum occur simultaneously in almost all of the oil fields in the world gives an interesting but unsolvable problem to scientists, but gives a cause of great annoyance to the workers of petroleum industry. Though no apparent relationship may exist between brine water and petroleum, yet their mysterious intimacy in nature tells us some intrinsic relation between them, and if this would be brought to light, the mystery concerning the origin of petroleum would probably be disclosed, and in consequence we would have some important clue which must be of great service to the discovery of petroleum deposit. This thought led some of the earlier petroleum geologists and chemists to their earnest studies of brines from different oil fields and to give rise to several theories of their origins. Prior to any other investigators, Hunt[1] in 1875 suggested from his study of the brine water from Ontario that it comes from the ancient sea water embedded simultaneously with the formation of the petroleum deposit. In 1905 Lane[2] extended this idea more generally and published a well-known theory named the connate or fossil water theory, which states that the brine water from an oil field is no other than the ancient sea water secluded from the outer side and preserved in strata of earth. On the other hand, Washburne[3] and Richardson[4] have somewhat different opinions that the salts contained in brine water have not their origin in those

of the sea water as the forementioned investigators believed, but in some other salts which might come from easily soluble basic magmas or salt deposits. These opinions, however, do not seem to be adequate at least in Japan whose geological conditions differ from those in foreign countries. It may therefore be mentioned here that the acceptable theories at present are those which stand on sea water, though in particulars they are differently modified by many investigators.

Analyses of the Japanese Brine and the Discussion of Their Results. The present authors who have had much interest in the co-existence of brine and petroleum for a long while had an opportunity to get the brines from widely different oil fields in Japan for which there have been little known in the literature. The brines taken for the analyses are those from the oil fields in Akita and Niigata Prefectures and that from the natural gas field with an oil indication in Chiba Prefecture. The results of the analyses are shown in Table 1, where the composition is given in molar ratios taking the sodium as 100%. Column 8 shows the absolute concentration of the sodium (grams per litre) in each brine for reference. Parallel to Table 1, Table 2 shows the composition of the sea waters from several places in the world which are all quoted from other authors. As seen from Table 1 and Table 2, it is clearly understood that the composition of sea waters give as already considered quite concordant values to each other independent of their occurring places, and that of brines are also, though not fairly concordant, yet roughly convergent to certain definite ratios in spite of the diversity in their geological distribution. Remarkable similarities are found between the composition of the sea water and that of the Japanese brine water in the ratios of the sodium, potassium and calcium, but far less quantities are observed in the magnesium and sulphate in the case of the brine, especially the latter being a trace or naught. The chlorine also seems to have somewhat lower values in the brine. As for the minute content of the sulphate in the brine from oil fields which is true not only for Japan, but also for any other countries, many explanations have been proposed by foreign investigators: Höfer[9] and Rogers[10] by whom the former's theory was supported, proposed that the lack of the sulphate may be due to the interaction between brine water and petroleum in the following chemical change:

$$SO_4^{--} + CH_4 \rightarrow CO_3^{--} + H_2O + H_2S,$$
$$\text{or} \rightarrow S^{--} + 2H_2O + CO_2$$

The idea was rejected by Palmer[11] who stated that these reactions, being endothermic, can not be well explained unless some favorable con-

Table 1. Composition of Japanese brines.

Brines from	Na	K	Ca	Mg	Cl	SO_4	Na	Authors
1 Innai, Akita Pref.	100	2.16	0.82	1.67	105.2	0.01	4.69	Ishikawa & Baba
2 Michikawa, Akita Pref.	100	0.21	5.34	5.31	110.8	0.01	6.00	,,
3 Niizu, Niigata Pref. (Mean of 2 samples)	100	2.32 (3.02 1.62)	1.16 (1.63 0.68)	0.73 (1.15 0.30)	79.1 (82.6 75.6)	0.01 (0.02 0.00)	4.40 (4.76 4.03)	,,
4 Nishiyama, Niigata Pref. (Mean of 4 samples	100	0.32 (0.35 0.27)	1.91 (2.62 1.57)	0.49 (0.61 0.40)	95.1 (101.7 90.7)	0.00	6.72 (7.28 6.16)	,,
5 Ôtaki, Chiba Pref.	100	1.17	0.74	1.14	102.3	—	9.75	,,
6 Katsurane, Akita Pref. (Mean of 6 samples)	100	2.42 (4.27 1.09)	1.88 (6.70 0.31)	0.96 (2.51 0.30)	104.2 (117.4 79.1)	0.12 (0.36 0.02)	4.16 (8.05 1.02)	Mikawa[3]
7 Ôtaki, Chiba Pref. (Mean of 6 samples)	100	0.87 (1.96 0.62)	0.77 (1.46 0.23)	2.86 (4.53 0.92)	89.0 (109.5 54.6)	—	2.67 (6.40 0.88)	Ôhashi[6]

(1) The Asahi Oil Co.'s well, 381.5–385.5 m. deep, at Innai-mura, Yuri-gun, Akita Prefecture.

(2) The Asahi Oil Co.'s well, 162 m. deep, at Michikawa-mura, Yuri-gun, Akita Prefecture.

(3) The Asahi Oil Co.'s well, 93 m. deep, of Aozawa, Take, Niizu-cho, Niigata Prefecture and the same Co.'s well, 270 m. deep, at Okubozawa, Take, Niizu-cho, Niigata Prefecture.

(4) The Nippon Oil Co.'s wells, No. 33, 880 m. deep; No. 24, 771 m. deep; No. 60, 1200 m. deep; and No. 35, 1228 m. deep, at Taka-machi, Kariha-mura, Kariha-gun, Niigata Prefecture.

(5) The Ôtaki Natural Gas Co.'s No. 2 well, at Oyamatsu, Fusamoto-mura, Isumi-gun, Chiba Prefecture.

Parenthesized figures show the highest and lowest values respectively.

Table 2. Composition of sea waters.

Seas	Na	K	Ca	Mg	Cl	SO_4	Br	Na
Mean of 77 samples collected during the voyage of Challenger	100	2.12	2.25	11.50	117.2	6.02	0.176	10.77
Between Cape of Good Hope and England (Mean of 22 samples)	100	2.07	2.36	12.17	118.2	6.26	0.170	10.99
Near Carthage, Mediterranean	100	2.11	2.33	11.33	118.6	6.10	0.171	11.84
Black Sea (Mean of 6 samples)	100	2.24	2.66	11.61	117.3	5.87	0.170	6.17
Red Sea (Mean of 4 samples)	100	2.06	2.31	11.39	119.7	5.91	0.171	16.58
Genkai-Nada, Sea of Japan[7]	100	2.18	2.35	11.33	114.9	5.96	—	10.11
Inland Sea, Japan[8]	100	2.02	2.03	11.76	117.4	6.12	—	10.12

Table 3.

Composition of animal bloods (sera or plasmas).

Animals	Na	K	Ca	Mg	Cl	SO_4	Authors
Medusa: Aurelia flavidula	100	3.05	2.37	10.81	120.3	3.79	Macallum[14]
Horseshoe crab: Limulus polyphemus	100	3.31	2.33	10.59	121.3	3.83	,,
Lobster: Homarus americanus	100	2.19	2.78	1.63	111.0	1.92	,,
Sharks: Acanthias vulgaris	100	2.71	1.56	2.33	107.5	—	,,
Mustelus canis	100	1.63	1.89	1.07	87.8	0.96	Smith[15]
,,	100	2.07	2.15	1.11	85.2	0.66	,,
Carcharias littoralis	100	2.13	1.94	0.89	88.4	0.12	,,
,,	100	1.96	2.18	0.84	87.6	0.25	,,
Rays: Raja stabuloforis	100	1.91	1.45	0.65	88.6	trace	,,
,,	100	1.91	1.23	1.02	97.5	trace	,,
,,	100	2.04	1.49	1.37	92.2	0.20	,,
,,	100	—	1.69	1.31	99.6	trace	,,
Raja diaphenes	100	2.87	2.15	1.48	95.8	1.31	,,
Fishes: Lophius piscatorius	100	3.48	1.74	0.50	95.0	0.60	,,
,,	100	3.76	2.10	8.07	112.4	1.99	,,
,,	100	4.39	1.02	0.68	81.0	1.76	,,
,,	100	3.42	1.09	—	89.1	1.14	,,
Gadus callarias	100	2.72	2.78	2.11	87.8	—	,,
,,	100	5.59	2.26	1.33	97.1	—	Macallum[14]
Pollachius virlus	100	2.55	1.78	1.38	89.4	—	,,
Amiataus calva	100	1.29	4.54	0.30	90.9	1.06	Smith[15]
,,	100	1.73	3.46	0.30	89.5	2.26	,,
Lepidosteus osseus	100	1.93	4.36	0.21	84.3	1.71	,,
Turtles: Chrysemys marginata	100	2.50	5.08	6.58	67.7	—	,,
,,	100	2.42	3.22	1.07	59.9	0.54	,,
Graptemys geographia	100	1.94	2.74	0.40	69.8	0.32	,,

Table 3.—(*Concluded*).

Animals	Na	K	Ca	Mg	Cl	SO_4	Authors
Turtles: Emys blandingii	100	3.00	2.54	1.62	70.0	1.00	Smith[15]
Pseudemys elegans	100	2.62	3.33	3.49	64.1	0.08	,,
Chelydra serpentina	100	2.48	4.61	3.19	38.7	0.21	,,
,,	100	2.22	3.22	1.43	54.4	0.21	,,
Caretta kempi	100	4.05	3.19	0.86	66.4	0.18	,,
Caretta caretta	100	4.44	2.05	1.92	72.7	—	,,
Dog	100	3.97	1.43	0.83	84.2	—	Abderhalden[16]
,,	100	3.49	1.47	0.72	82.4	—	,,
Cat	100	3.89	1.37	0.75	82.0	—	,,
,,	100	3.94	1.24	0.87	66.1	—	Baumann & Kurland[17]
Rabbit	100	3.84	1.45	0.80	76.0	—	Abderhalden[16]
Ox	100	4.00	1.42	0.75	74.6	—	,,
Pig	100	4.18	1.59	0.74	74.5	—	,,
Horse	100	3.84	1.41	0.81	73.2	—	,,
Man	100	3.42	1.71	0.86	69.2	1.37	Kramer & Tisdall[18]

dition of thermochemical or geochemical action should occur.

Mills and Wells[12] considered the diminution of the sulphate in the brine to be due to the adsorption of it by some colloidal particles charged with positive electricity.

Recently Bastin[13] elucidated the same phenomenon by the action of micro-organisms whose metabolism necessarily consumes the sulphate in the brine.

Although the above explanations may prove the natural tendency of the unusual diminution of the sulphate in the brine, they can not interpretate the variation of the elements whose contents differ much from the contents in the sea water. In fact, little attention has been hitherto made in regard to the comparatively small content of the magnesium in the brine.

Taking the substantial differences between the sea water and the Japanese brine in consideration, the authors hesitate to accept the con-

nate water theory which necessitates the introduction of some other assumptions of different viewpoints in order to elucidate the fact. It must be remembered that a question whether or no the ancient sea water was possessed of the same composition as the contemporary one remains unsettled. This question is no doubt of interest from the geological and biological standpoints, but also of importance from the authors' viewpoint at the same time, as will be shown later on.

In 1910 Macallum[14] put forward an interesting suggestion to this problem. He proposed, having analysed the inorganic constituents in the bloods of several animals (1) that the inorganic blood composition of an animal of a certain genus is entirely invarient ever since that genus took the first appearance on the earth and (2) that the inorganic blood composition of an animal created as an ancester of a genus must be identical with that of the surrounding sea water at that time in order to be suited to environments. Table 3 shows the inorganic composition of blood sera or plasmas of various kinds of animals in the same expressions as taken in Table 1 and Table 2. The comparison of Table 3 with Table 2 which shows the composition of sea waters brings us that there exists some dissimilarity between them except the jelly-fish and horseshoe crab. The exceptional cases seen in the jelly-fish and horseshoe crab were regarded by Macallum as such, with a reason that they have incomplete excretory organs which admit sea water to pass through their bodies freely.

In the authors' opinion, however, his conception for the sea water of olden times seems to be wrong from the consideration of the paleontological fact that the jelly-fish appeared already in Cambrian formation and the horseshoe crab somewhat later but its larva quite resembles to the trilobite which appeared likewise in Cambrian, and it is highly probable to assume that the inorganic blood composition of these animals may indicate no other than the composition of the ancient sea water, and that, that of the other animals which appeared far later than these have no such composition as that of the ancient sea water on account of their gradual development of organs.

It is also plausible from a geological standpoint of view that the composition of the ancient sea water did not differ so much from the to-day's so far as it is concerned to the sea water of a relatively new period such as Tertiary, when almost all of the petroleum deposits in Japan were formed.

From what has been stated above about the ancient sea water, the authors are convinced that the Japanese brine at least would not be

the same as the sea water in its origin, but something other as it will be discussed in the following.

Existing Theories of the Origin of Petroleum in Japan. Now it is a matter of great importance to look upon the theories hitherto published on the origin of petroleum in Japan which must be closely related to the origin of brine. Among the theories of the origin of Japanese petroleum the two theories are commonly accepted, one being proposed by Takahashi[19] the other by Kobayashi.[20] According to Takahashi the organogenetic rocks which are found at oil strata in Japan may be the origin of petroleum because they always contain a minute quantity of kerosene often with a plenty of fossils of planktons, fishes and seaweeds, and these occurrence gave rôle of the formation of the brine water from the sea water whose composition differed little from the contemporary sea water. Although his idea for the brine water seems to surpass any other preceding theories in probable modification of the connate water theory instead of others' assuming the gradual transformation of the sea water into the brine with somewhat ambiguous changes, the brine as he considers is that which contains a large amount of alkaline earth elements such as the calcium and magnesium, whose phenomenon however is not the case in the Japanese brine as seen from Table 1. Kobayashi insisted on the so-called fish oil theory of the origin of the Japanese petroleum from the experimental facts of his own and coworkers i.e. fish oils yield petroleum-like hydrocarbons on dry distillation with Japanese acid clay at relatively low temperature and pressure. His theory is favorably accepted for the reason (1) that the distribution of the oil fields in Japan superposes approximately on that of the places producing acid clay and (2) that the oil fields can be considered to have situated at the seasides of the old times, where fishes were abundant. That the petroleum may be yielded from fish oils by the action of the acid clay only is not fully recognized, but that fish oils may be attributed to its origin is of some truth. In view of geological evidence most of Northern Honshiu of Japan was yet unseen on the sea in the early Tertiary age and fishes propagated in abundance owing to hotter climate than that of to-day as it is easily imagined, when occurred subsequent revolutions on land and sea which caused fishes to gather[21] near the seaside and to be buried under ground resulting in the formation of petroleum.

Grün and Wirth[22] who also supported the fish oil theory came to the conclusion that among fishes elasmobranchs are most probable as its origin because of the facts (1) that the livers of these fishes are

commonly large as compared with their bodies and contain a great amount, 70–90% of the total, of a higher terpentine-like hydrocarbon "squalene" named by Tsujimoto,[23] (2) that this yields hydrocarbons of great resemblance to natural petroleum by thermal decomposition and (3) that elasmobranchs were prosperous in the age of petroleum formation.

Independent of these investigators Tanaka and Kuwata[24] separated, with naphthenic acid, from the petroleum from Ishikari in Hokkaido, Niigata and Akita Prefectures some saturated fatty acids such as palmitic, myristic, stearic, and arachidic among which the first acid being predominant, and found that the relative amounts of these fatty acids are almost identical with those in whale oil, shark liver oil, herring oil, or cod oil. They claimed from these facts that the animals which are most probable as the origin of petroleum may be the shark or whale in consideration of their inhabitation.

To these concordant results obtained by different investigators which lay stress on the fish especially of elasmobranchs oil theory the present authors will add an important suggestion resulting directly from the analyses of the Japanese brine from oil fields.

Similarity in the Compositions of the Brine and of the Fish Blood. The great resemblance between the composition of the Japanese brine and that of the bloods of fishes especially of elasmobranchs may be reasonably understood if we assume that the brine from an oil field comes from neither the sea water nor any underground water as the existing theories do, but from the body fluids of abundant corpses of fishes especially of elasmobranchs which are squeezed out by the compressive action of the earth crust, whose oily part being converted into petroleum at the same time.

The fact that the lack of the sulphate in the brine is simply explained by assuming as its origin elasmobranchs whose blood is lacking in the sulphate is of interest when we refer it to the rôle of sulphur compounds in the metabolism in the blood of higher animals. Indeed, elasmobranchs appeared already in Devon or Carboniferous ages while the other sea fishes in Jurassic and later ages.

According to Abderhalden[16] the inorganic composition of blood serum or plasma is not identical with that of blood corpuscle in the case of a higher animal such as the horse, pig, rabbit and man, and therefore it makes no estimation of the total inorganic blood composition from that of blood serum or plasma only. The blood corpuscles of these animals contain more potassium but less sodium than the blood sera or

plasmas which are shown in Table 3. As for a sea animal Macallum[14] found that the total blood of the whale contains much potassium as the horse or pig does. Other higher animals such as the dog, cat, sheep, ox, deer, and etc., however, have no remarkable differences in the compositions of sera (or plasmas) and corpuscles, and such tendency would be the less, the lower an animal such as fish is. Smith's[15] results indicated on this point that the body fluids of fishes are very similar in inorganic composition with their blood sera or plasmas. From the above elucidation, the authors' hypothesis that the Japanese brine would come from the blood of fishes especially of elasmobranchs may be easily accepted, consistent with the fish oil theories of the origin of petroleum proposed by Tanaka and Kuwata and by Grün and Wirth. But the whale taken as the origin by the former authors must be rejected from the above Macallum's result.

As it has been often reported[25] that a comparatively large amount of iodine and bromine were found in the analyses of brine waters, the authors have determined these contents as well as the other constituents already shown. The result are shown in Table 4, in which the contents of these elements in the sea water observed by Fellenberg[26] and etc. are also shown. As seen from this table the molar ratios of bromine of the brine and of the sea water have no difference between them, while the iodine of the former is from 500 to 3000 times as much as that

Table 4.

Iodine and bromine contents of the Japanese brine and of the sea water.

	Iodine	Bromine	Authors
Brine from Innai, Akita Pref.	0.096	0.27	Ishikawa & Baba
Brine from Michikawa, Akita Pref.	0.015	0.16	,,
Brine from Niizu, Niigata Pref.	0.028	0.12	,,
Brine from Nishiyama, Niigata Pref.	0.037	0.26	,,
Brine from Ôtaki, Chiba Pref.	0.051	0.11	Ôhashi[6]
Sea water	0.000031	0.17 (Mean, from Tab. 2)	Fellenberg[26]

Table 5.

Iodine content of bloods of mammals.

Mammals	Iodine content $\times 10^6$ gr.%	Authors
Man	11.0	Turner[27]
,,	13	Kendall[27]
,,	8—12.8	Veil & Sturm[28]
Dog	11.1	Turner[27]
Sheep	4.1—1.5	Mauer & Ducrue[29]
Rabbit	3.1—0.7	,,

of the latter. The probable sources of such a considerable amount of iodine contained in the brines are perhaps due to marine lives, but the comparison of iodine content of the bloods of different animals with those of the brines can not unfortunately be done here because no appreciable data of fishes are found in the literature. In Table 5 the iodine content of a few mammals are given. Though somewhat low values are recorded in the cases of the sheep and rabbit, the iodine content of the bloods of mammals in general may be considered of the same order. Adopting the value 198 mg.% obtained by Kramer and Tisdall[18] as one of the probable values for the absolute sodium content in the human blood, the molar ratio of the iodine to the sodium is calculated to be 0.0010, which is much greater than that of the sea water (0.000031) but still smaller than that of brines (0.015–0.096).

Now, for fishes no such comparison can be made, but it is a well-known fact[30] that fishes especially elasmobranchs contain richer iodine than any other higher animals do, and it is also evident from the study of Mauer and Ducrue[29] that their bloods are rich in iodine when considered their foods. As regards the bromine content in the animal bloods no much mention is possible, but according to Bernhardt and Ucko[31] human blood contains from 1.0 to 1.5 mg.% in the normal state, which is equivalent to the molar ratio from 0.15 to 0.22, this indicating that the bromine content is perhaps universally constant in the animal bloods, the sea water and the brine.

If there is truth in what has been discussed for the origin of the brines, the brines from the same oil zone may have a constant or at least a similar composition with each other and conversely if under-

ground water has a composition of the known brine type, it may give an oil indication together with a help of geological inquiry. On this hypothesis, the authors have examined mineral waters widely occurring in Japan whose analyses were completely carried out by the Imperial Hygienic Laboratories.[32] Among more than five hundred kinds of hot or cold mineral waters they have picked up three kinds of cold waters very similar to the brine type, whose composition is shown in Table 6 in the same expressions as before: The first is at Nagano in Niigata Prefecture, situated near Ômo, a famous oil field in the same Prefecture, the second is at Onishika, situated within the circumscription of the well-known Rumoi oil field in Teshio of Hokkaido. These two must of course be included in the same type of the brines shown in Table 1. The third is at Kashio in Nagano Prefecture where there has had as yet no production of petroleum, but an oil indication is beyond question according to the generally accepted geological opinion that it is situated on the famous Itoigawa-Shizuoka fault line, along which may exist the elongation of the great petroleum zone of northern part of Japan.

Table 6.

Composition of mineral waters of the brine type in Japan.

Mineral waters from	Na	K	Ca	Mg	Cl	Br	I	SO_4
1 Nagano, Niigata Pref.	100	0.55	1.77	3.18	100.7	0.10	0.010	0.015
2 Onishika, Hokkaido	100	0.93	3.50	2.37	105.8	0.11	0.034	—
3 Kashio, Nagano Pref.	100	0.83	3.25	0.66	108.9	0.04	trace	trace

NOTE:
(1) Nagano, Morimachi-mura, Minamikambara-gun, Niigata Prefecture.
(2) Onishika-mura, Rumoi-gun, Teshio Province, Hokkaido.
(3) Kashio, Oshika-mura, Shimoina-gun, Nagano Prefecture.

Conclusion. From the above results the authors have come to the conclusion that the Japanese brine from oil fields have a certain type of composition which is remarkably similar to the inorganic blood composition of fishes, especially of elasmobranchs and that this fact can be reasonably explained by assuming that the origin of the brine from oil fields are the body fluids of these fishes whose oils have been known to be most plausible as the origin of petroleum. Though the mechanism of the formation of petroleum as well as of brine water from the corpses of these fishes can not be fully accounted for, the above considerations will be of service to the investigation in the line.

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EINFLUSS DES NATRIUM-, BARIUM- UND ALUMINIUM-CHLORIDS AUF DIE HYDROLYSE DES EISENCHLORIDS BEI ÜBER 100°C.

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Die Hydrolyse des Eisenchlorids bei über 100°C wurde schon von verschiedenen Autoren untersucht, aber die Änderung der Hydrolyse des Eisenchlorids durch Anwesenheit von Fremdsubstanzen scheint noch nicht studiert zu sein. Als ein einfaches Beispiel zu diesen Fällen beobachtete ich die Reaktion, die bei Erhitzung der drei Mischungen, (A) $FeCl_3+NaCl$ (B) $FeCl_3+BaCl_2$ und (C) $FeCl_3+AlCl_3$, auf über 100°C stattfindet. NaCl, $BaCl_2$ und $AlCl_3$ wurden als Repräsentanten der uni-, di- und trivalenten Verbindung ausgewählt.

In der vorliegenden Arbeit wird der schon in einer früheren Abhandlung beschriebene Autoklav angewendet.(1) Nachdem die gewünschte Temperatur darin erreicht ist, wird das Erhitzen noch eine Stunde fortgesetzt. Über das Verfahren ist auch schon damals Genaueres gesagt worden. Die Mischung wird so hergestellt, dass die Konzentration der beiden Substanzen in (A), (B) und (C) 0.25N ist, z.B. besteht die Mischung (A) aus je 10 ccm 0.5N $FeCl_3$ und 0.5N NaCl. Für jede Mischung ist neu hergestellte Lösung des Eisenchlorids angewendet worden.

Dabei ist ein Platintiegel von einem Volumen von ca. 25 ccm mit Platindeckel benutzt worden, in der Annahme, dass das Platin für den vorliegenden Versuch am zweckmässigsten sei. Eine schematische Skizze des Autoklavs mit Untersatz für den Platintiegel ist in der folgenden Figur gegeben. Die Mischungen (A), (B) und (C) wurden bei 120°, 140° und 160°C geprüft.

(A) *0.25N in $FeCl_3$ und in NaCl und* (B) *0.25N in $FeCl_3$ und in $BaCl_2$.*

Bei 120°C und noch bei 140°C sedimentierte gelber Niederschlag auf dem Boden des Tiegels. Es ist erst bei 160°C gelungen, hämatitähnlichen Niederschlag zu erhalten.

(C) *0.25N in $FeCl_3$ und in $AlCl_3$.*

Schon bei 140°C fand der hämatitähnliche Niederschlag statt. Die

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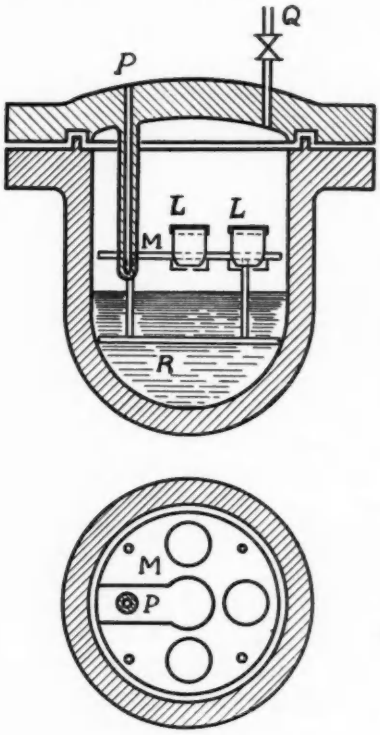

Querschnitt des Autoklavs.

Skala: ca. $^1/_5$ der natürl. Grösse

L: Platintiegel

M: Untersatz

P: Höhlung für den Thermometer

Q: Hahn

R: Wasser

Lösung 0.25N $FeCl_3$ zerfiel auch bei 140°C in Hämatit (Fe_2O_3) mit HCl, wovon das erstere auf dem Boden sedimentierte und das letztere den oberen klaren flüssigen Teil bildete.[1] Bei 160°C zeigten 0.25N $BaCl_2$ und auch 0.25N $AlCl_3$ keine Spur des Zerfalls.

Zusammenfassung.

Es wurde der Einfluss des NaCl, $BaCl_2$ und $AlCl_3$ auf die Hydrolyse des $FeCl_3$ bei über 100°C studiert. Dabei wurde beobachtet, dass NaCl und $BaCl_2$ die Hydrolyse störten, d.h. die notwendige Temperatur für den volkommenen Zerfall des $FeCl_3$ erhöhte sich durch die Anwesenheit dieser Substanzen. Das $AlCl_3$ übte bei der Hydrolyse des $FeCl_3$ keinen merkbaren Einfluss auf die Temperatur aus.

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